

APPLICATION OF STABLE CARBON ISOTOPE ANALYSIS
TO CONTINUOUS COAL/OIL COPROCESSING

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INTRODUCTION

Stable carbon isotope analysis is a promising technique for distinguishing and quantifying the individual contributions of the coal and petroleum feedstocks to coprocessing products. Such information is valuable for process modeling and optimization and for discerning reaction pathways and interactions between the two feedstocks. Carbon isotope analysis provides information only on the fate of carbon; however, this is a minor limitation because most products are 85-90% carbon. A potentially significant obstacle to accurate quantitation is selective isotopic fractionation, a phenomenon by which the two stable carbon isotopes from a single feedstock selectively report to different products. Selective isotopic fraction appears to be exacerbated by reaction severity, and it can cause large quantitation errors at high conversion conditions unless some means is employed to correct for it. This paper describes the isotope analysis of samples from a continuous coprocessing bench-unit run performed by Hydrocarbon Research, Inc. (HRI) with Maya vacuum still bottoms (VSB) and Taiheiyo (Japanese) coal at high conversion conditions. A method to correct for selective isotopic fractionation was employed that allowed quantitation of the conversions of the individual feedstocks.

BACKGROUND

Fifteen product oils and two feedstocks were obtained from S. V. Panvelker, of HRI, from HRI continuous coprocessing bench Run 238-2, also known as Bench Run 4. Run 238-2 was a 25-day feedstock reactivity test performed with Maya VSB and Taiheiyo coal. The run was completed in November 1988. Six sets of operating conditions (1,2), each lasting 4 or 5 days, were used during the run, as illustrated in Table 1. The principal variables were oil to MF coal ratio, space velocity, temperature, and catalyst age. Recycle was used only during the 1/1 oil/coal periods. Product yields (2,3) are reported in Table 2. The product samples obtained included five fractions of the net products from each of periods 5, 13, and 25 (conditions 1, 3, and 6, respectively). The fractions included initial boiling point (IBP) by 350°F, 350 by 650°F, and 650 by 975°F distillates, 975°F+ solubles, and unwashed pressure-filter solids. Samples of the two feedstocks also were obtained. Sample size ranged from 10 to 50 g for each sample. Carbon content was determined on each sample with a LECO CHN-600 instrument. Carbon isotope analyses were performed in duplicate on each sample at the Stable Isotope Laboratory of Conoco Inc. in Ponca City, Oklahoma. Carbon isotope ratios and carbon contents of all samples appear in Table 3. The chemical analysis of the coal appears in Table 4.

DISCUSSION

Through use of the isotope ratios and a simple mixing equation, one can calculate the coal carbon/total carbon ratio of each product. Such an approach assumes that there is no selective fractionation of the isotopes, or at least that it is small

enough to be ignored. Uncorrected results, which appear in Table 5, show an over-accounting of coal carbon, presumably from selective fractionation.

Though gas and insoluble organic matter (IOM) samples were not received for analysis, their delta values and carbon contents can be estimated by forcing carbon and carbon isotope balances to 100%. This was done as follows: The pressure-filter solids (PFS) contain entrained oils (lower half of Table 2). The overall yields were adjusted to include the PFS by substituting the PFS for appropriate amounts of each component in the overall yield. Yields and carbon and isotope analyses were thus available on all products except the gas, which was then forced. With the forced gas data so obtained, the IOM data could be forced. The forcing calculation method is detailed elsewhere (4). Several comments on the results from this exercise, which appear in Table 6, are in order. The forced carbon contents of the gases appear reasonable in light of their composition (Table 2). The negative uncorrected coal carbon contents calculated for the gases merely reflect their light (more negative) isotopic composition. This is to be expected and has been observed in those cases for which gas samples actually were analyzed. Of course, the negative values have no physical meaning; they merely reflect isotopic fractionation. The IOM fractions have quite small yields, reflecting the high coal conversions (ca. 95% MAF). The uncorrected calculated carbon contents of the IOM fractions are not fully reasonable; for example, the Condition 1 IOM has more carbon than total mass. This reflects the combination of all errors. The errors in IOM carbon contents are actually quite small on an absolute basis, being less than 1% in all cases. The uncorrected calculated coal carbon contents of the IOMs indicate that their carbon content is virtually all coal-derived.

As noted, the isotope analyses of the product fractions actually analyzed result in an overabundance of coal carbon when not corrected. This overabundance results from the high yields (15-18%) of isotopically light gases (ca. -30.4 per mil from forced balances). Even though the carbon content of the gases is only about 40 to 50%, they still account for 8 to 9% of the total carbon in the feedstocks. A first-order correction to the data can be applied by assuming that the carbon contained in the gases is formed from the petroleum and coal in proportion to the petroleum carbon and coal carbon in the feedstock. The fraction of the petroleum carbon and coal carbon that is not converted to gas then, has an isotope ratio that is heavier (less negative) than the whole petroleum and coal feeds, respectively. The correction method used here relies on three assumptions: 1) the carbon in the gas is formed from the two feedstocks in proportion to the carbon fed to the unit from each feedstock, 2) the difference between the $\delta^{13}\text{C}$ of each feedstock and the $\delta^{13}\text{C}$ of the gas produced from that feedstock is the same for the coal and the petroleum, and 3) the non-gas-producing carbon undergoes no further selective isotopic fractionation. The calculation method used to make this correction is detailed elsewhere (4). With this correction approach, we calculate delta values of the non-gas-producing petroleum carbon to be -26.88, -26.82, and -26.80 per mil for Conditions 1, 3 and 6, respectively; the average value is -26.84 ± 0.04 per mil. The non-gas-producing coal carbon is calculated to have delta values of -23.75, -23.68, and -23.66 per mil, respectively, for the same periods, with an average delta value of -23.69 ± 0.05 per mil. The calculated delta values of the petroleum gas and coal gas average -31.46 and -28.32 per mil, respectively.

Carbon sources, selectivities, and conversions of the non-gaseous products are shown in Table 7 on the basis of the corrected delta values. Selectivity is the enrichment of coal carbon/total carbon in a product relative to the whole feedstock. Carbon sources are plotted in Figure 1, coal carbon conversions are plotted in Figure 2, and petroleum carbon conversions are plotted in Figure 3. The following observations concern the corrected results from Table 7 and Figures 1

through 3. The coal carbon to total carbon ratio in the condensed product fractions increases with boiling point with the one exception of the 975°F+ soluble product. The selectivity data (Table 7) indicate that the IBP x 350°F and 350 x 650°F products are selectively produced from petroleum. The 650 x 975°F and IOM products are selectively produced from coal. The 975°F+ solubles are produced from the two feedstocks without selection. The IOM carbon is close to being entirely coal-derived. In Condition 3, the IOM carbon is calculated to be more than 100% coal-derived; as noted earlier, this error appears to be associated with the need to determine the IOM properties by forced carbon and isotope balances. As expected, all fractions show the greatest coal carbon contributions during Condition 3, which was operated at a 1/1 petroleum/coal ratio. Conditions 1 and 6 were identical (except for catalyst age), including a 2/1 petroleum/coal ratio, and coal carbon contributions are quite similar for their respective products.

The major coal product is the 650 x 975°F distillate (Figure 2); 35 to 42% of the coal carbon reports to that fraction. The coal carbon conversions to IOM (3.4 to 5.8%) indicate that the total conversion of coal carbon to solubles was 94 to 97%. The major petroleum product is the 350 x 650°F distillate (Figure 3); about 38% of the petroleum carbon reports to that fraction. Very little of the petroleum carbon reports to the IOM product.

Interestingly, there is very little difference in conversions of the individual feedstocks between the run periods at petroleum/coal ratios of 2/1 (Conditions 1 and 6) and at 1/1 (Condition 3). Though other operating conditions (T, SV) also were changed, this suggests that within the precision of the data there is no synergy between the feedstocks for conversion, or at least that the degree of synergy is unchanged at ratios of 1/1 and 2/1.

SUMMARY

The analytical results show that selective isotopic fractionation was severe enough during HRI Run 238-2 that accurate carbon source quantitation and individual feedstock conversions cannot be obtained without correcting for isotopic fractionation. A first-order correction was applied that assumes that the feedstocks each fractionate into two "pools" of differing isotopic composition: the gas and the condensed products. The results support the validity of the correction method employed. The petroleum more readily produces light products. Its major product is the 350 x 650°F distillate, whereas that of the coal is the 650 x 975°F distillate. The insoluble organic matter (IOM) is nearly all coal-derived and the naphtha is mostly petroleum-derived. The 975°F+ soluble product is produced in proportion to the feedstock blend. There is no evidence for synergistic interactions between the two feedstocks with respect to conversion to products.

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TABLE 1
OPERATING CONDITIONS: HRI COPROCESSING RUN 238-2

Condition	1	2	3	4	5	6
Period	1-5	6-9	10-13	14-17	18-21	22-25
Oil to MF Coal Ratio	2	1	1	2	2	2
Recycle-to-Fresh-Feed Ratio	0	0.5	0.5	0	0	0
Relative Space Velocity	1	1	1.6	1.6	1.6	1
Temp., °F (1st and 2nd Stage)	810	810	825	825	810	810

Feedstocks: Taiheiy coal; Maya VSB

Catalysts: Commercial Ni/Mo on alumina, both stages, batch aged during run.

Source: Reference 1, and for temperatures and catalyst, Reference 2.

TABLE 2
PRODUCT YIELDS: HRI COPROCESSING RUN 238-2

Condition	1	2	3	4	5	6
Period	5	8/9	13	-	-	25
<u>Yields, wt % of dry feed</u>						
H ₂ O, H ₂ S, NH ₃	8.63		9.32	-	-	8.09
CO	0.05	11.0	0.16	-	-	0.06
CO ₂	0.03		0.09	-	-	0.05
C ₁ x C ₈	4.89	5.5	5.18	-	-	3.97
C ₄ x C ₇ (in gas)	3.52		3.19	-	-	2.97
IBP x 350°F	12.91		12.72	-	-	13.41
350 x 650°F	32.82	34.7	28.53	-	-	31.05
650 x 975°F	26.57	21.2	24.90	-	-	25.96
975°F+ Solubles	9.59	9.2	11.48	-	-	11.19
IOM	0.88	1.9	1.94	-	-	1.42
Ash	4.27	6.4	6.41	-	-	4.27
H ₂ Consumption	-4.16	-4.4	-3.88	-	-	-3.37
Sum(a)	100.00	100.1	100.04	-	-	99.07
<u>Performance, wt % MAF</u>						
Coal Conversion	-	95.6	-	-	-	-
975°F+ Conversion	-	87.5	-	-	-	-
<u>Composition of Unwashed Pressure-Filter Solids, wt % of dry feed</u>						
650°F-	0.10	-	0.41	-	-	0.17
650 x 975°F	1.45	-	3.74	-	-	3.24
975°F+ Solubles	0.63	-	2.11	-	-	1.84
IOM	0.88	1.9	1.94	-	-	1.42
Ash	4.27	6.4	6.41	-	-	4.27
Total	7.33	-	14.62	-	-	10.94

(a) Sums may not equal exactly 100.00% because of slightly different calculation methods used by HRI to arrive at these gas and liquid yields.

Source: Reference 3 and, for Condition 2 data, Reference 2.

TABLE 3
CARBON ISOTOPE RATIOS AND CARBON CONTENTS

	Operating Condition	$\delta^{13}\text{C}$, per mil avg. \pm std. dev. (b)	Carbon wt % (d)
<u>Feedstocks</u>			
Taiheiyo Coal (HRI #5595)	All	-24.12 \pm 0.02	68.36(d)
Maya VSB (HRI #5567)	All	-27.26 \pm 0.02(c)	85.75
<u>Products</u>			
IBP x 350°F	1	-26.50 \pm 0.01	85.41
350 x 650°F	↓	-26.14 \pm 0.06	87.38
650 x 975°F		-25.75 \pm 0.04	87.54
975°F+		-25.88 \pm 0.01	91.11
Pressure Filter Solid(a)	↓	-25.08 \pm 0.14	47.96
IBP x 350°F	3	-25.70 \pm 0.03	85.10
350 x 650°F	↓	-25.70 \pm 0.06	87.76
650 x 975°F		-24.98 \pm 0.11	88.10
975°F+		-25.54 \pm 0.01	89.57
Pressure Filter Solid(a)	↓	-24.84 \pm 0.09	47.06
IBP x 350°F	6	-26.29 \pm 0.03	85.77
350 x 650°F	↓	-26.19 \pm 0.07	87.32
650 x 975°F		-25.51 \pm 0.01	88.01
975°F+		-25.90 \pm 0.06	91.18
Pressure Filter Solid(a)	↓	-25.42 \pm 0.01	51.09

(a) Unwashed.

(b) All isotope analyses performed in duplicate at Conoco's Stable Isotope lab.

(c) Original duplicate set of analyses gave -26.20 and -26.86 per mil; however, analyst noted that he could not obtain a representative sample for that pair of analyses. Repeat duplicate analysis are shown.

(d) Reported on an as-determined basis for all samples, except for coal which is reported on a MF basis.

TABLE 4
ANALYSIS OF TAIHEIYO COAL

Moisture, wt % as determined	4.59
Proximate, wt % dry basis	
Volatile Matter	49.26
Fixed Carbon	38.60
Ash	12.14
Ultimate, wt % dry basis	
C	68.36
H	5.69
N	1.02
O (diff)	12.50
S, total	0.27
pyritic	0.07
sulfate	<0.01
organic (diff)	0.20
Cl	0.019
Ash	12.14
Gross Cal. Value, dry, Btu/lb	12,239

TABLE 5
UNCORRECTED COAL CARBON AS PERCENT OF TOTAL CARBON
HRI COPROCESSING RUN 238-2

<u>Product</u>	<u>Operating Condition</u>	<u>Coal Carbon/ Total Carbon, %(b)</u>
IBP x 350°F	1	24.2 ±0.6
350 x 650°F	↓	35.7 ±2.0
650 x 975°F		48.1 ±1.4
975°F+		44.0 ±0.6
Pressure Filter Solid(a)	↓	69.4 ±4.5
IBP x 350°F	3	49.7 ±1.1
350 x 650°F	↓	49.7 ±2.0
650 x 975°F		72.6 ±3.5
975°F+		54.8 ±0.6
Pressure Filter Solid(a)	↓	77.1 ±2.9
IBP x 350°F	6	30.9 ±1.1
350 x 650°F	↓	34.1 ±2.3
650 x 975°F		55.7 ±0.6
975°F+		43.3 ±2.0
Pressure Filter Solid(a)	↓	58.6 ±0.6

(a) Unwashed.

(b) Standard deviation reflects random error but not bias errors.

TABLE 6
PROPERTIES OF GASES AND IOM PRODUCTS BASED ON MASS, CARBON,
AND ISOTOPE BALANCES: HRI COPROCESSING RUN 238-2

<u>Run Condi- tion</u>	<u>Yield, lbs Product/ 100 lbs Dry Feed</u>	<u>lbs Carbon in Product/ 100 lbs Dry Feed</u>	<u>lbs Coal Carbon in Product/ 100 lbs Dry Feed (Uncorrected)</u>	<u>Coal Carbon/ Total Carbon Ratio (Uncorrected)</u>	<u>δ¹³C, per mil</u>
<u>Hypothetical Gases</u>					
1	17.12	6.66	-6.68	-100.25	-30.41
3	17.94	7.64	-6.89	- 90.20	-30.09
6	15.14	7.37	-8.06	-109.36	-30.69
<u>Hypothetical IOM</u>					
1	0.88	1.58	1.55	97.61	-24.20
3	1.94	1.34	1.70	126.98	-23.27
6	1.42	0.91	0.91	99.71	-24.13

TABLE 7
CORRECTED CARBON SOURCES, SELECTIVITIES AND CONVERSIONS
HRI COPROCESSING RUN 238-2

Product	Run Condi- tion	Coal Carbon as a % of Total Carbon (a)	Selectivity for Coal Carbon (b)	Conversion of Coal C to Fraction, %	Conversion of Petroleum C to Fraction, %
Hypothetical Gas	1	28.5	1.0	8.3	8.3
1BP x 350°F		10.8	0.4	5.2	17.2
350 x 650°F		22.2	0.8	28.0	39.0
650 x 975°F		34.6	1.2	35.3	26.6
975°F* Solubles		30.5	1.1	11.7	10.6
Hypothetical IOM		<u>93.8</u>	<u>2.9</u>	<u>5.8</u>	<u>0.4</u>
Total		-	-	94.3	102.1
Hypothetical Gas	3	44.4	1.0	9.9	10.0
1BP x 350°F		36.9	0.8	11.7	15.9
350 x 650°F		36.9	0.8	27.0	36.8
650 x 975°F		60.2	1.4	38.6	20.4
975°F* Solubles		42.1	0.9	12.7	13.9
Hypothetical IOM		<u>115.8</u>	<u>2.6</u>	<u>4.5</u>	<u>0.5</u>
Total		-	-	104.4	96.5
Hypothetical Gas	6	28.5	1.0	9.2	9.2
1BP x 350°F		17.5	0.6	8.8	16.6
350 x 650°F		20.6	0.7	24.6	37.7
650 x 975°F		42.2	1.5	42.3	23.1
975°F* Solubles		29.8	1.0	13.4	12.5
Hypothetical IOM		<u>86.0</u>	<u>3.0</u>	<u>3.4</u>	<u>0.2</u>
Total		-	-	101.7	99.3

(a) Petroleum carbon as % of total carbon is 100% minus this value.

(b) Selectivity is calculated as the ratio of coal carbon/total carbon in a product fraction to the coal carbon/total carbon ratio in the whole feedstock.

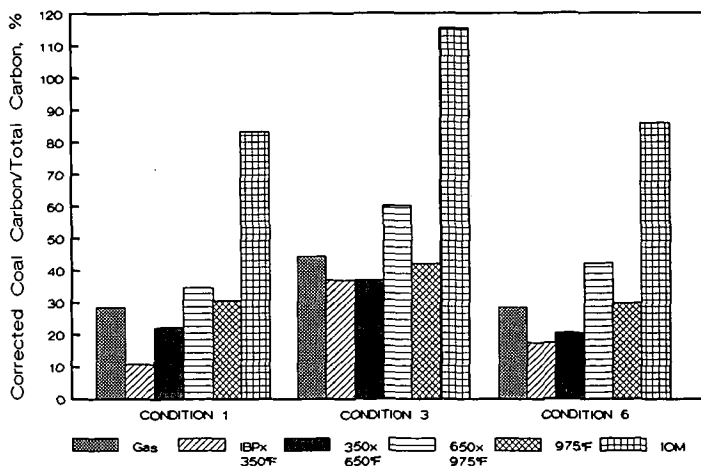


Figure 1. Corrected Coal Carbon to Total Carbon Ratios Plotted vs Run Condition. HRI Run 238-2.

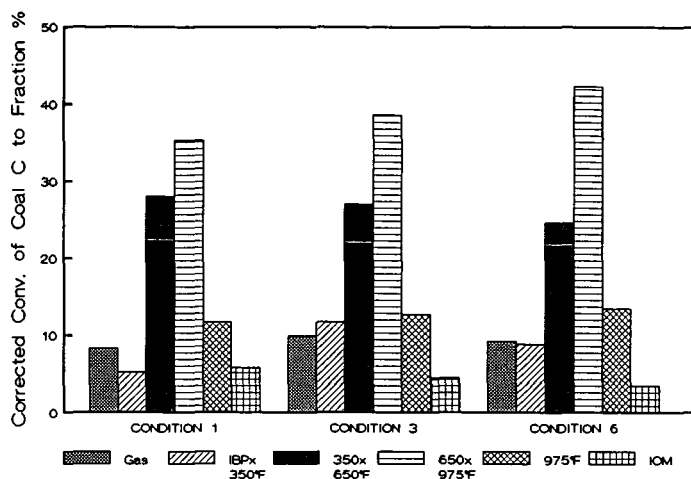


Figure 2. Corrected Conversions of Coal Carbon Plotted vs Run Condition. HRI Run 238-2.

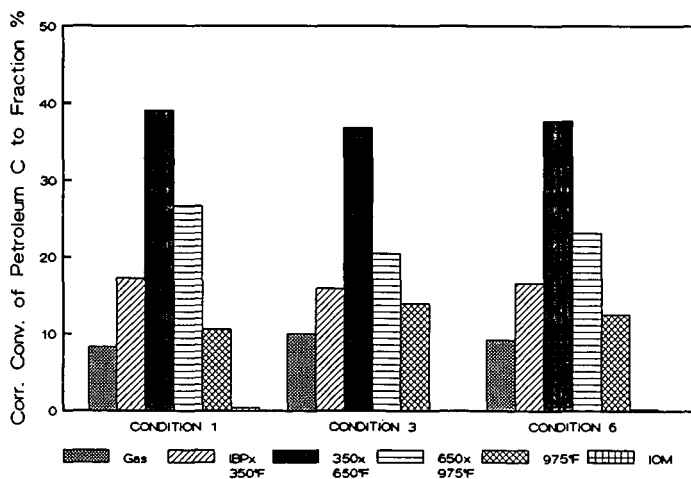


Figure 3. Corrected Conversions of Petroleum Carbon Plotted vs Run Condition. HRI Run 238-2.